

Direct Observation of the Oxygenated Species during Oxygen Reduction on a Platinum Fuel Cell Cathode

The performance of polymer-electrolyte-membrane (PEM) fuel cells is limited by the reduction at the cathode of various oxygenated intermediates in the four-electron pathway of the oxygen reduction reaction. A research team led by SLAC scientists performed x-ray spectroscopy identification and DFT simulations of oxygenated intermediates on a platinum fuel-cell cathode (Figure 1). They demonstrate that, during the oxygen reduction reaction, hydroxyl intermediates on the cathode surface occur in several configurations with significantly different structures and reactivities. The ambient pressure x-ray photoelectron spectroscopy (APXPS) on SSRL Beam Line 13-2 directly probed the correlation between the species on the surface and the electrochemical potential. Based on density functional theory calculations, the scientists show that the removal of hydration enhances the reactivity. Tuning the hydration of hydroxyl near the triple-phase boundary will be crucial for designing more efficient fuel-cell cathodes.

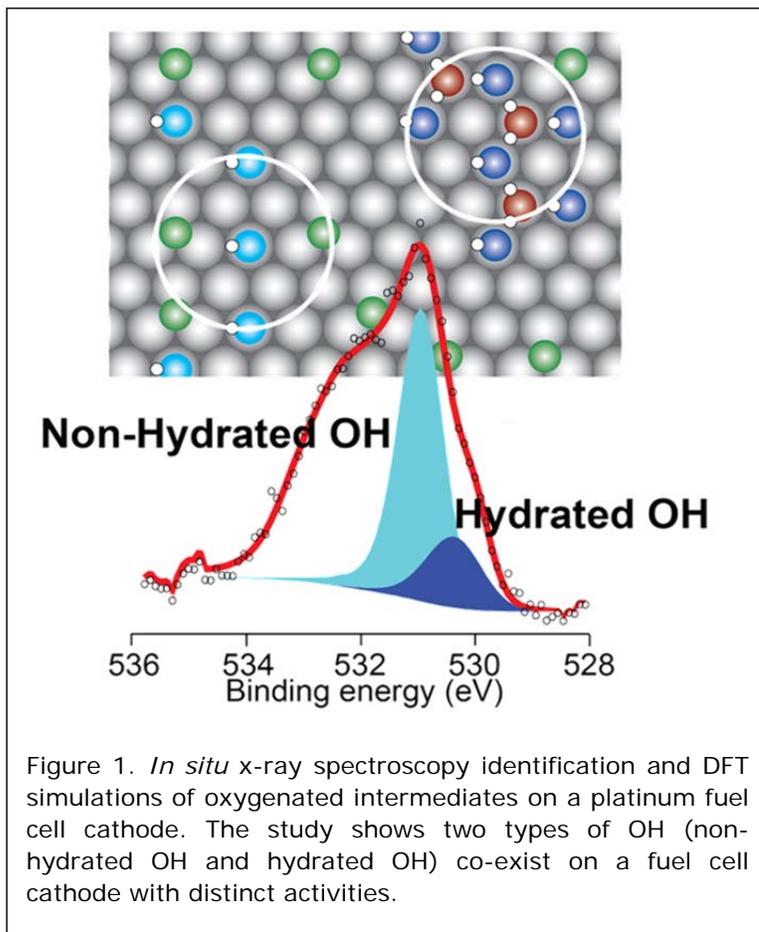
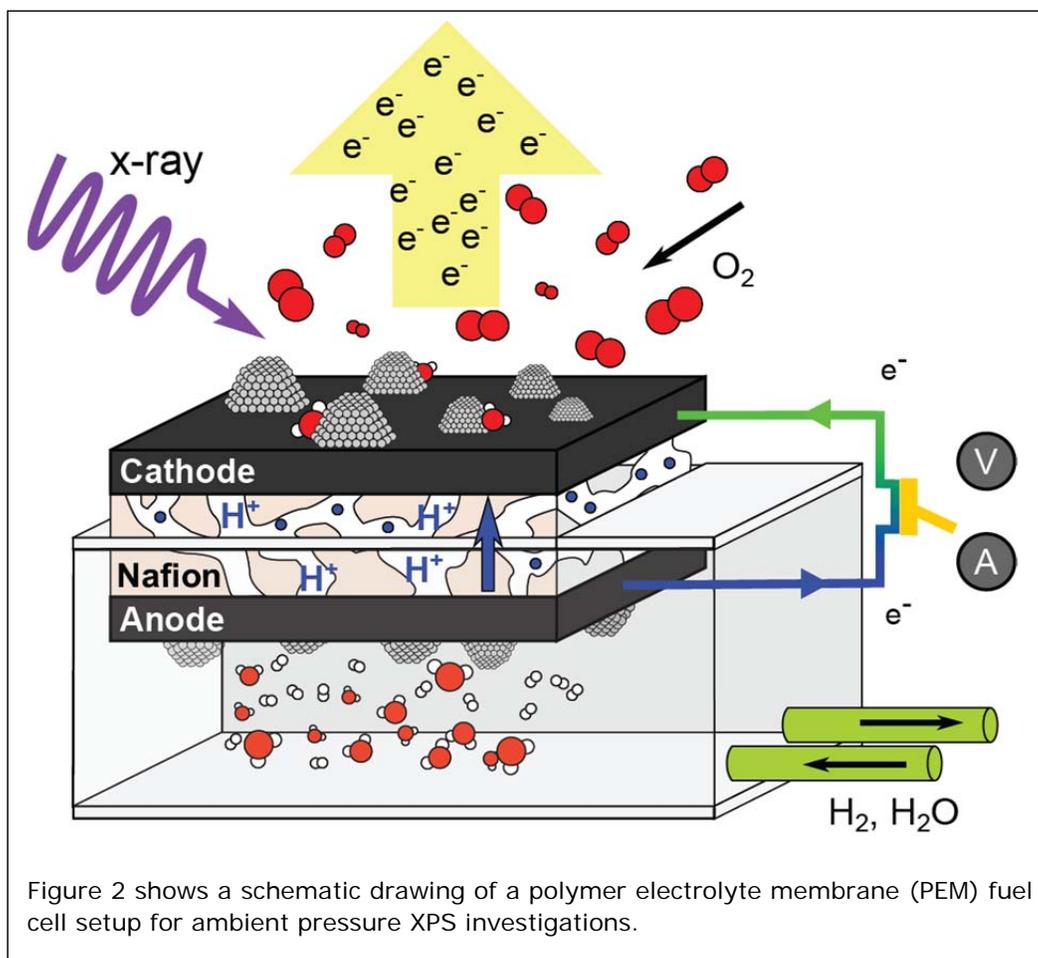


Figure 1. *In situ* x-ray spectroscopy identification and DFT simulations of oxygenated intermediates on a platinum fuel cell cathode. The study shows two types of OH (non-hydrated OH and hydrated OH) co-exist on a fuel cell cathode with distinct activities.

In this work, the scientists designed a PEM fuel cell (Figure 2) compatible with the APXPS system. To date, APXPS has been applied to the study of high-temperature solid-oxide fuel cells but not to PEM fuel cells. The electrochemical cell has a polymer membrane, which serves as an electrolyte, coated on both sides with carbon-supported platinum nanoparticles. The cathode side of the assembly was exposed to the APXPS gas cell, which was filled with oxygen gas. The anode chamber was filled with humidified forming gas. By connecting both electrodes to an external voltmeter or galvanometer, researchers can simultaneously record both XPS and either cell voltage or cell current.

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